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# FLAME INHIBITION RESEARCH QUARTERLY PROGRESS REPORT

1 August, 1960 - 31 October 1960

## YEARLY SUMMARY 1 November, 1960 - 31 October, 1961

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SUMMARY OF PROGRESS 1 August - 31 October 1961

- (1) A temperature profile was measured on the spherical stoichoimetric methane-oxygen-argon flame system whose composition structure was reported in TG 331-2.
- (2) The diffusion coefficient of the system A-H<sub>2</sub> (trace) was measured at atmospheric pressure over the range 300-1070°K.
- (3) An analysis was made of the effect of added HBr on fluxes and rates on the stoichoimetric methane flame. This indicated that a significant fraction of the reaction occurred on the surface of the ball. The principle effect of the added HBr appears to be the shifting of the methane reaction to appreciably higher temperatures.

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# FLAME INHIBITION RESEARCH

## I. BACKGROUND MATERIAL

### REPORT ORGANIZATION

This report is divided into four sections: I. Background Material, II. Program Outline, III. Summary of the program to the beginning of the reported quarter, and IV. Quarterly Progress. Only the fourth section contains new material (although Section III is updated quarterly). It is hoped that the background material will aid the unfamiliar reader in following the program without extensive references. Those who are familiar with the work may find it profitable to turn directly to the fourth section (Page 9).

### PROGRAM OBJECTIVE

The objective of this program is to obtain a scientific understanding of the mechanism of chemical inhibition of flames. Although this research is primarily restricted to the fundamental aspects of the problem, there are several potential practical by-products. A quantitative understanding of flame inhibition should allow the prediction of the relative effectiveness of inhibitors on a flame system from their known chemical kinetics. Thus, a rational initial choice of inhibitor should be possible without extensive empirical studies. (This factor may become of increasing importance as "exotic" fuels become common.) It would also seem possible to set an absolute upper limit for the effect of an inhibitor, so that their efficiencies can be evaluated.

### HISTORICAL SUMMARY

Over the past two decades, a number of studies have been made on flame inhibition of hydrocarbon-oxygen flames by halogen-containing compounds (Refs. 1 and 2). The experimental evidence suggests that the effectiveness of these materials is due to an effect on the chemical reactions in such flames. It has been established that the inhibition is a function of the concentration of the halogen, and that the order of effectiveness of the halogens is inverse to the reactivity of the free atoms, i.e.,  $F < Cl < Br < I$ . Most practical extinguishers contain bromine compounds. Iodine compounds are usually unstable and expensive.

It is generally accepted that the mechanism for such flame inhibition is the exchange reactions between the inhibitor and the free radicals that are responsible for the primary propagation reactions in flames. Such reactions lead to the formation of stable molecules and free halogen atoms, which are much less reactive than the flame radicals. In hydrocarbon-oxygen flames the important radicals are hydrogen atoms, oxygen atoms, hydroxyl radicals, and possibly methyl radicals. Other radicals exist in flames, but these are probably less important to the flame propagation. On this hypothesis one would expect that the following reactions would be important in flame inhibition:

- 1)  $RX + H\cdot \rightarrow HR + X\cdot$
- 2)  $RX + OH\cdot \rightarrow ROH + X\cdot$
- 3)  $RX + O_2 \cdot \rightarrow RO\cdot + X\cdot$

Here, R represents a hydrogen or hydrocarbon radical, and X represents a halogen. Dots indicate unpaired electrons. Reactions of this type are well known (Ref. 3), but much of the available data is too fragmentary to allow extrapolation of the kinetic information from the low-temperature regime of most laboratory studies to radical reactions at the high temperatures encountered in flames.

- 
1. R. Friedman and J. R. Levy, "Survey of Fundamental Knowledge of Mechanisms by Action of Flame Extinguishing Agents," WADC Tech. Report 56-568, Jan. 1957, Supplement I, Sept. 1958, Supplement II, April 1959.
  2. W. A. Rosser, H. Wise, and J. Miller, "Mechanism of Combustion Inhibition by Compounds Containing Halogen," Seventh Symposium (International) on Combustion, pp. 175-82, Butterworths Scientific Publications, London (1959).
  3. E. W. R. Steacie, Atomic and Free Radical Reactions, Reinhold Publ. Co., New York (1954) (2 volumes).

# FLAME INHIBITION RESEARCH

## II. PROGRAM OUTLINE

The research program will utilize studies of the detailed microstructure of flames (Ref. 4) with and without added inhibitor, together with such other chemical and physical studies as seem necessary to elucidate the detailed mechanisms of chemical inhibition of flames. The relation between these studies can be visualized in Fig. II-1. Following this figure the report will be divided into five major sections (flame structure studies, simple reaction studies, analysis, interpretation, and recommendations of flame inhibition), and eight minor sections (temperature profiles, composition profiles, aerodynamic profiles, and atomic and free-radical composition profiles). This is a long-range program of modest scale whose completion is expected to take from three to five years. Therefore, although work is planned in all of these categories, current work will usually occupy only a few of these sections.

The number of possible inhibitors and the number of possible flame systems are both large, and the number of flame-inhibitor systems which may be of interest is even larger since it is the product of these two numbers. The situation can be represented by a very large "matrix" in which one index of the terms represents the flame system and the other represents the inhibitor system. (See Fig. II-2). Since it is impractical to study such a large number of systems, two possible approaches suggest themselves: The synthetic method, in which one would study the chemistry of inhibitors with radicals, and a separate study of the uninhibited flame systems. This is equivalent to studying the initial row and initial column in the "matrix". A satisfactory theory would allow the prediction of the effect of any inhibitor on any flame from this information. The other approach is the statistical technique, which is often used in agriculture. Studies would be made of a randomized set of these systems using one of the patterns of experiment design, such as the Latin square. By studying this fraction of the systems, a satisfactory theory should allow the derivation of information sufficient to predict the effect of any specific inhibitor on any specific flame system.

Both approaches assume that an adequate theory is developed. Therefore, a judicious combination of these two approaches seems in order. Early studies should be aimed at developing a theory, subsequent studies should be aimed at making a randomized statistical test of the efficacy of the theory, and final studies should be aimed at the accumulation of data. On this basis we propose to make a very detailed study

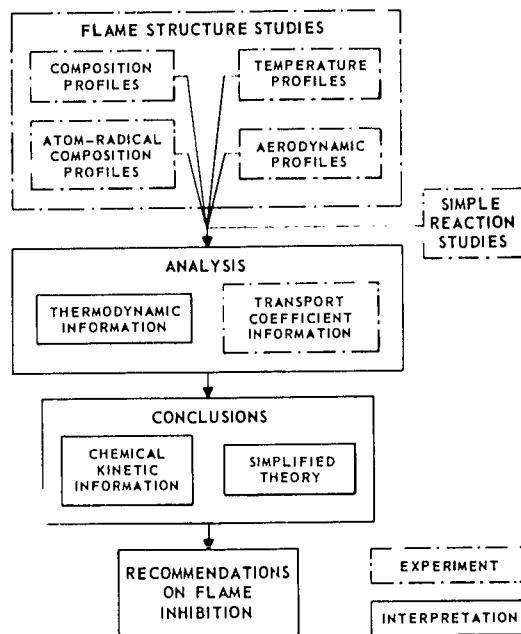
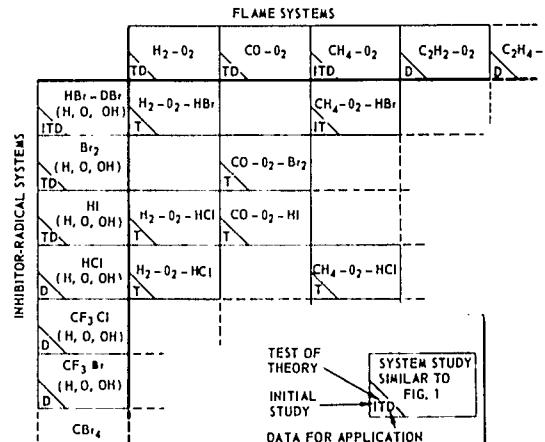


Figure II-1 FLOW OF INFORMATION IN THE PROGRAM TO STUDY FLAME INHIBITION



Initial Study, I - An intensive study of one inhibitor-flame system is directed toward the goal of a simplified theory of flame inhibition. The chosen system is methane-oxygen with HBr (and/or DBr) as an inhibitor.  
 Test of Theory, T - The theory from the initial study should then be tested on representative inhibitor-flame systems to confirm its generality.  
 Data for Application, D - If the theory seems satisfactory, then a store of data should be developed to permit its broad application. Such data is most readily obtained from simple systems - the flame systems alone and inhibitor-radical reaction systems. The required data include those of chemical kinetics, transport coefficients, and thermodynamic properties.

Figure II-2 OVER-ALL PROGRAM TO STUDY FLAME INHIBITION

4. R. M. Friedman, and W. G. Bert, "Program for the Study of Flame Inhibition", proposal submitted by the Johns Hopkins University Applied Physics Laboratory, in response to USAEC Request for Cooperators, October 1960.

of the methane-oxygen flame with a simple inhibitor (probably HBr) to develop the theory. This will be followed by a randomized test on a restricted number of systems, and finally by a systematic study of parameters. The program is illustrated by Fig. II-2. It is discussed in more detail in Ref. 4.

### FLAME STRUCTURE EXPERIMENTAL STUDIES

It is planned to use flame structure techniques in this research, on flames both with and without inhibitors. These techniques have been discussed in the literature (Refs. 5 and 6) and offer certain advantages for studying chemical reactions: 1) flames offer a steady-state for study, 2) there is no wall problem, 3) there are no mixing problems for studying fast reactions. The disadvantages are: 1) data analysis is complex and, 2) high precision is required of the data for obtaining kinetic information. These techniques nevertheless offer an excellent method for studying fast, high-temperature reactions and, in particular, offer the ideal technique for studying flame inhibition reactions *in situ*.

To characterize a flame system, it is necessary to specify at least  $N + 1$  variables, where  $N$  is the number of molecular species (Ref. 5). The independent variable usually chosen is distance through the flame front, while the dependent variables are composition, temperature, velocity, or area ratio. Experimentally, it is common to classify the profiles in four categories according to the techniques required to measure them. These are: composition profiles, atomic and free-radical composition profiles, temperature profiles, and aerodynamic profiles. An example of such a set is given in Fig. II-3.

#### Composition Profiles

From the chemical standpoint, the most important information is the concentration profiles. The most satisfactory technique developed for making such studies is the microprobe sampling technique, which is followed by mass spectral analysis. The technique consists of withdrawing a sample of gas from the flame using a small, tapered quartz probe. The probe can be made small enough so that its effect on the flame is negligible, and the low pressure and rapid pressure drop in such a tapered probe quenches the sample so that reproducible meaningful samples can be obtained. Radical concentrations are not obtained by these techniques and are discussed in the next section. This technique is discussed in detail in the literature (Ref. 7).

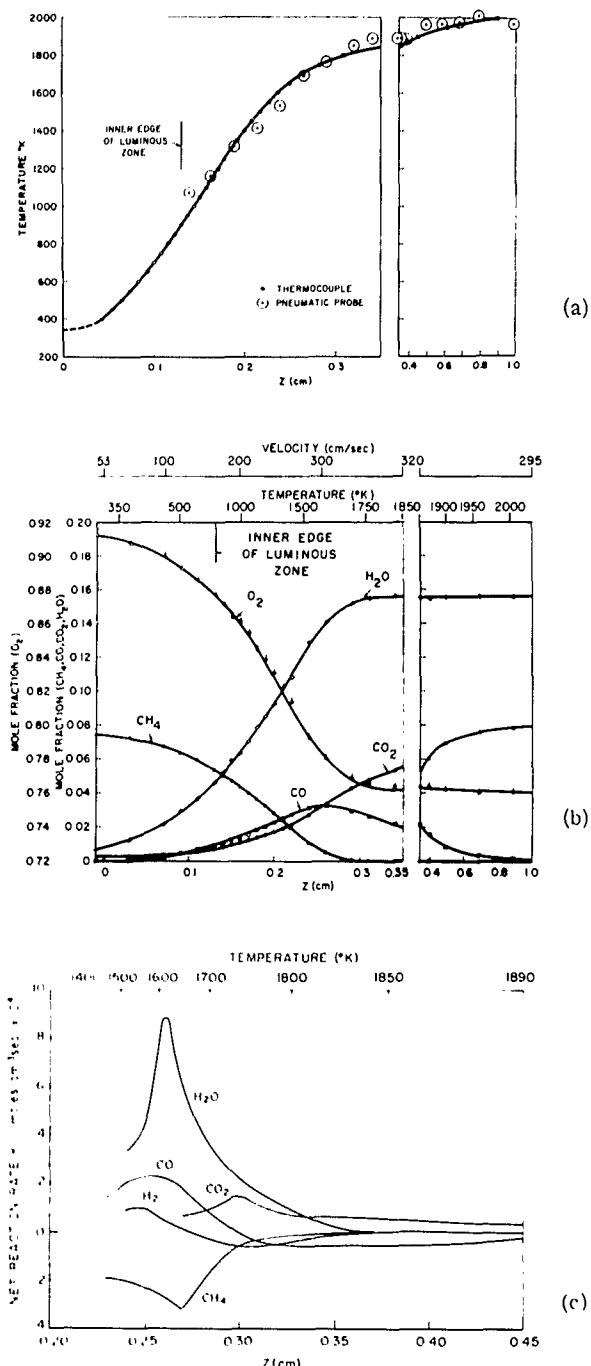


Figure II-3 CHARACTERISTIC PROFILES FOR A METHANE-OXYGEN FLAME.

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4. J. W. Dantzig, "Structure of Luminous Flames," *Sixth Symposium (International) on Combustion*, p. 111, Academic Press, New York (1957).
5. J. W. Dantzig, *Introduction to Flame Theory*, McGraw-Hill Book Company, New York, 1966.
6. J. W. Dantzig, *Experimental Flame Structure I - Characteristics of the Premixed Methane-Oxygen Flame*, *Combustion Letters*, 1, 1 (1964).

### Radical-Atom Concentration Profiles

Logically, atom-radical concentration flame studies are part of the concentration profile determinations. However, since their study requires special techniques, they are considered separately.

Radicals and atoms are not susceptible to conventional sampling techniques because of their extreme reactivity which transforms them into stable species before analysis is possible. In most flame structure studies (Refs. 5 and 7) these concentrations are considered (usually correctly) to be negligible compared with the concentrations of the stable species, and are therefore neglected in the analysis. This reasonable approximation is, of course, only a stopgap measure to obtain information while satisfactory methods are developed for determining atom and radical concentrations. None of the techniques thus far developed (Refs. 8 through 10) possess the generality and spatial resolution necessary for the quantitative interpretation which we wish to make. Therefore, we are developing a new technique for studying radical concentration profiles under a companion flame structure study supported by ARPA (Task R). This is the scavenger probe method, which combines the techniques of probe sampling with those of chemical scavenging. A sample is taken through a probe, and the radical-containing gases are mixed rapidly with a large excess of a suitable "scavenger" gas which reacts with the radical to produce a characteristic product. Scavenger studies are well known in radiochemistry and photochemistry (Ref. 11), and mass spectrometer studies (Ref. 12) have indicated that radicals can be sampled successfully through orifices.

An absolute measurement of concentration can be made if 1) there is a one-to-one correspondence between the reaction product and the precursor radical and, 2) the analytical system (mass spectrometer) can be calibrated for the stable reaction product. This is a significant advantage since it is notoriously difficult to obtain absolute radical concentrations. Spatial resolution will be limited by the probe diameter, and sensitivity should be as high as the analytical system allows for stable species. As this technique is developed it will be used in these studies.

### Temperature Profiles

Temperature profiles offer an important technique for characterizing flame fronts. Three methods have been used at this Laboratory: thermocouple traverses, aerodynamic measurements, and pneumatic probe measurements. Their data are in essential agreement (Ref. 6), although of varying precision.

The most precise method is that with thermocouple traverses in which temperatures are measured with fine (0.0005") Pt-Pt 10% Rh thermocouples coated with silica. Profiles with a precision of 10°K and excellent spatial reproducibility are obtained.

Temperature can be determined by using aerodynamic measurements of velocity and area ratio, deriving the point-by-point density through the continuity relations, and then applying the perfect gas law. The results are not of high precision (2-4%), but within their limits, they provide a reliable measure of the translational temperature of the gas.

Temperatures can also be measured with a pneumatic probe (Ref. 13). This device is a quartz probe similar to those used in the composition studies. If gas flows under choking conditions through two orifices in series, and the temperature is known at the second orifice, temperature at the inlet orifice of such a probe can be derived from the relation between ambient pressure and the pressure between the two orifices. This technique provides a moderately precise (1-2%) and reliable method for determining temperature and has the added advantage that it can be directly associated with a composition, since it can also be used for composition sampling.

### Aerodynamic Profiles

Flames can be characterized aerodynamically by two profiles - velocity and area ratio. As mentioned under temperature measurements, these can be combined to derive a density profile. The area ratio is simply the geometry of the stream tubes of flow through the flame front. In the general case it is necessary to make this measurement, since stream tube expansion through

- 
7. R. M. Fritsch, "Experimental Determination of Radical Concentrations in Flames", APL JET CM-974.
  8. C. G. James and J. R. Sutler, "Thermometric Investigations of Alkali Metals in Hydrogen Flame Gases I - A General Survey of the Use of Ionization Radiation in the Measurement of Atomic Concentration", Proc. Roy. Soc. A-247, p. 141 (1958).
  9. W. E. Kunkel, "Hydroxyl Concentration in Hydrogen-Air Flames Held on Porous Burners", Comb. and Flame, 1, 259-255 (1958).
  10. T. Grewer and H. G. Werner, "Die Reaktionsrate von Flammen", Zeit. fur Phys. Chem. (Bere. Folge) 52, 511-517 (1959).
  11. R. H. Schuler, "Scavenger Methods for Free Radical Detection in Hydrocarbon Radiolysis", J. Chem. Phys., 30, 37-41 (1959).
  12. S. Foner and R. Hudson, "The Detection of Atoms and Free Radicals in Flames by Mass Spectrometric Techniques", J. Chem. Phys., 31, 155-159 (1959).

the flame is appreciable. With a symmetrical flame, such as the spherical flame, it is unnecessary to make this measurement, since it can be obtained directly from the geometry of the position determinations. Direct aerodynamic measurements are made by introducing MgO particles as a tracer and photographically visualizing their paths through the flame front, using a Zr flashbulb for the stream tube measurements and a pulsed electronic flashlamp for the direct velocity measurements (Ref. 14).

### SIMPLE REACTION STUDIES

Flame systems have relatively complex chemistry (see Table I) which makes the identification of the dominant reactions difficult. For this reason it is desirable to supplement the flame studies with studies of the individual reactions with simplified chemistry. A second reason for doing so is that these studies will be made at lower temperature, thus enabling more precise estimates to be made of the activation energy.

The activation energy of most flame reactions lies below 10 kilocalories per mole, so that at flame temperatures the rate is a very insensitive function of the activation energy. On the other hand for this very reason, flame studies allow an accurate determination of the steric factor and may ultimately allow a determination of its temperature dependence - a problem which has plagued chemical kineticists for many years.

The techniques we propose to use are the conventional discharge tube-mixing techniques, with the addition of direct measurement of radical concentrations using the scavenger probe technique being developed. This work has been summarized by Steacie (Ref. 3) to 1954. More recent work has been carried out by a number of authors (Ref. 15).

### DATA ANALYSIS

To make quantitative interpretation of flame structure information it is necessary to analyze the data. An analysis consists of calculating the actual flux profiles and rate of species and heat production profiles by quantitatively accounting for the effects of molecular diffusion and thermal

Table I  
Methane-Oxygen Flame Reaction Kinetic Constants

Reaction	Activation Energy, E (kcal mole <sup>-1</sup> )	Frequency Factor, A (10 <sup>14</sup> cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	8.5	2
$\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$	8	2*
$\text{CH}_3 + \text{O}_2 \rightarrow \text{OH} + \text{H}_2\text{CO}$	0	1
$\text{H}_2\text{CO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	0	2
$\text{HCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}$	0	2
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	7	0.3
$\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$	25	1
$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	18	5
$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	10	1
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	10	1
$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	0	-
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	18	5

\* The value given is an estimate, normal for this type of reaction.

conductivity. This step is necessary to avoid false impressions of the rate processes involved (Fig. II-3), since in many flames the effects of diffusion and thermal conduction are large.

This analysis is based on the flame equations consisting of conservation laws and the differential equations of transport and chemical kinetics. They have been formulated in generality by Hirschfelder (Ref. 16) and adapted for flame structure analysis by Westenberg (Refs. 17 and 18).

### Thermodynamic Information

The thermodynamic functions of interest are enthalpies, and heat capacities. This information is generally available for almost all of the species

13. C. Gutfelder, Jr., "Instrumentation for the Measurement of Local Flame Temperatures in High-Velocity Streams", *APL JOURNAL*, p. 117, 1951.
14. R. M. Fristrom, W. H. Avery, K. Prevette, and A. Matlack, "Flame Zone Studies by the Particle-Track Technique. I - Apparatus and Technique", *J. Chem. Phys.*, pp. 106-9 (1954).
15. Symposium on Some Fundamental Aspects of Atomic Reactions, *Can. J. of Chem.*, Vol. 38, October (1960), pp. 1045-7052.
16. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York, pp. 76-33, (1954).
17. R. M. Fristrom and A. A. Westenberg, "Flame Zone Studies IV - Microstructure and Material Transport in a Laminar Propane-Air Flame Front", *Comb. and Flame*, 217-8 (1957).

found in flame inhibition studies over the temperature range of interest. Several standard reference sources are available (such as Ref. 18) which provide data of sufficient accuracy for our purposes.

#### Transport Coefficient Studies

Transport coefficient information is necessary for the quantitative interpretation of flame structure data. The required data are the binary diffusion coefficients for the species being studied and the thermal conductivities of the mixtures. The multicomponent diffusion coefficients necessary for the interpretation of such systems are a complex function of all of the binary diffusion coefficients (Ref. 19). To avoid this problem it is usual to choose systems in which one species can be considered dominant; in this case, the true multicomponent diffusion coefficients can be accurately approximated by a set of binary diffusion coefficient of the individual species with the dominant species. The general case, with no single dominant species, could also be handled, but only at the expense of an order of magnitude increase in the necessary diffusion coefficient information (in the general multicomponent case, it is necessary to know the diffusion coefficients of all of the possible pairs of species) (Ref. 20).

The principal problem is to obtain precise, reliable data at sufficiently high temperatures to be useful in the flame studies. A new technique has been developed at APL which allows such measurements (Ref. 21). Diffusion coefficient data are available for the methane-oxygen system (Ref. 22).

The problem of thermal conductivities of mixtures is in a less satisfactory state, but fortunately this information is unnecessary for kinetic studies. An analogous "point source" technique is being developed at APL under Task R for making such measurements (Ref. 23).

#### INTERPRETATION

The interpretation of this information on flame structure consists of deriving chemical kinetic information and information on flame processes (Refs. 24 through 26). The analysis

provides data on rates and fluxes of enthalpy and the various molecular species. Such a description is unambiguous and complete, but if the information is to be useful on other systems it is necessary to deduce the detailed reaction scheme and derive the appropriate kinetic constants, activation energies and steric factors. This step is largely art, since in a real system all possible reactions occur to some extent. What is desired is to provide a description of the dominant reactions. For this reason there may be several interpretations with varying levels of sophistication and complexity. For flame inhibition work what is usually desired is the simplest possible interpretation consistent with a quantitative description.

#### Chemical Kinetic Information

Once a mechanism is assigned, the derivation of chemical kinetic data from flame structure and simple reaction rate information is straightforward. The choice of mechanism is largely a subjective process. We will not discuss the process other than to point out that a useful beginning is often a systematic collection of the possible reactions. The data which we have available from flame structure and simple reaction studies are: temperature, concentrations, and rates. The constants which are of interest are: the activation energy E, the steric factor P, and the temperature dependence of the steric factor n. In most kinetic studies, and probably in our initial work, the precision is not sufficient to allow separation of the temperature dependence factor from the exponential dependence of the activation energy. Flame studies, however, do offer information in a temperature regime which may ultimately allow such a separation to be made. If this is possible, it will represent an important addition to kinetic information. The relation of the exponential and power dependence of the reaction rate on temperature is best visualized by expanding the Arrhenius exponential factor as a series:

$$R_i = R_j X_i X_j Z P T^n e^{-E/RT} \\ = X_i X_j \frac{Z_0}{T_0} P \left\{ T^{n-1} - \frac{E^2}{R^2} T^{n-3/2} + \frac{E^2}{2! R^2} T^{n-5/2} + \dots \right\}$$

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- 18. K. A. Merten and F. V. Kistiakowsky, "Methane-Oxygen Flame Structure II - Conservation of Hydrogen Energy in the Methane-Oxygen Flame", *J. Phys. Chem.*, **63**, 1292-1298 (1959).
  - 19. F. D. Rossini, et al., *Selected Values of Physical and Chemical Properties of Hydrocarbons and Their Derivatives*, Bureau of Mines, Pittsburgh, Pa. (1955).
  - 20. R. E. Walker, et al., and K. A. Merten, "Measurements of Multicomponent Diffusion Coefficients in the C<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> System Using the Point-Source Technique", *J. Chem. Phys.*, **30**, 141-146 (1959).
  - 21. R. E. Walker and K. A. Merten, "Molecular Diffusion Studies in Methane at High Temperature I - The Point-Source Technique", *J. Chem. Phys.*, **31**, 112-120 (1959).
  - 22. R. E. Walker and K. A. Merten, "Molecular Diffusion Studies in Methane at High Temperature IV - Results and Interpretation of the C<sub>2</sub>O<sub>2</sub>-O<sub>2</sub>, CH<sub>4</sub>-O<sub>2</sub>, and H<sub>2</sub>O-O<sub>2</sub> Systems", *J. Chem. Phys.*, **32**, 46-53 (1960).

Since the species are interrelated, a number of cross checks should be possible on the derived kinetic constants, so that there will be a reasonable assurance of the essential correctness of the derived mechanism.

#### Simplified Theory

The goal of these studies is to provide a description of flame inhibition which is relatively simple and yet still will yield quantitative predictions. This may not always be possible, but it appears that in the case of the methane-oxygen flame a start can be made. The goal of such a simplified theory would be to enable quantitative predictions to be made of the effect of inhibitor on flame reactions (and hence burning velocity) with a precision of 20 per cent. In a sense this simply represents the limit of interpretations, since all mechanisms represent abstractions of the true system.

#### RECOMMENDATIONS OF FLAME INHIBITION

As a result of this work it is hoped that it will be possible to make some practical recommendations on flame inhibition. It is hardly possible to predict in advance what such recommendations will be, but it seems reasonable to expect that they will include recommendations of specific inhibitors for specific flame systems.

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23. R. E. Walker, H. deJarnett, and A. A. Westenberg, "New Method of Measuring Gas Thermal Conductivity", Phys. of Fluids, 3, 482 (1960).
  24. R. M. Fristrom, A. A. Westenberg, and W. H. Avery, "Etude du Mechanisme de la Reaction Propane-Air par l'Analyse de Profils de Fronts de Flamme", de l' Institut Francais du Petrole et Annales de Combustion Liquide, Vol. XIII, No. 4, pp. 544-53 (1958).
  25. A. A. Westenberg and R. M. Fristrom, "Methane-Oxygen Flame Structure IV - Chemical Kinetic Considerations", J. Phys. Chem. to be published Feb. 1961.
  26. R. M. Fristrom and A. A. Westenberg, "Experimental Chemical Kinetics from Methane-Oxygen Laminar Flame Structure", Presented at the Eleventh Symposium (International) on Combustion, Sept. 1960.

FLAME INHIBITION RESEARCH

III. SUMMARY OF PREVIOUS WORK

This material is included in the Yearly Summary;  
following the pink separation page at the back of this  
book.

"FLAME INHIBITION RESEARCH

IV. REPORT OF PROGRESS

1 AUGUST - 31 OCTOBER 1961

TEMPERATURE PROFILE

C. Grunfelder and R. Fristrom

A temperature profile was required to complete the information on the spherical methane flame ( $\text{CH}_4$ -0.090  $\text{O}_2$ -0.182 A-0.728; P=0.05Atm) on which HBr inhibition studies had been made (Ref. 1). Since the final temperature of this flame was higher than the melting point of platinum, it was not practical to use our usual Pt; Pt-10%Rh couples. To surmount this problem a new type (to this laboratory) of high temperature thermocouple was employed, Ir; Ir-10%Rh. This couple has recently been studied by the Bureau of Standards and accurate calibrations are available (Ref. 2). The material proved to be very satisfactory for micro-thermocouples. Junctions could be easily made using flame welding techniques and they can be easily coated with silica (Ref. 3). The wire is strong and stiff so that couples as fine as  $5 \times 10^4$  inches in diameter can be readily fabricated (this is difficult with the Pt; Pt-10%Rh wire).

The 0.0005" silica coated thermocouple was mounted on a micrometer drive mechanism. Positions were measured using a Gaertner microscope cathetometer. Voltages were measured using a 10 millivolt Brown Recorder. To establish the emissivity coefficient for the

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\*References for Section IV are on page 31.

coated thermocouple the final flame temperature was measured using a bright couple. The measured maximum temperature was  $2278^{\circ}\text{K}$ . The estimated emissivity correction for bright Ir  $35^{\circ}\text{K}$  bringing the probable final temperature so close to the calculated adiabatic value  $2325^{\circ}\text{K}$  that this value was assumed to evaluate the emissivity correction for the coated couple (Ref. 3).

The measured profile is shown in Fig. IV-1.

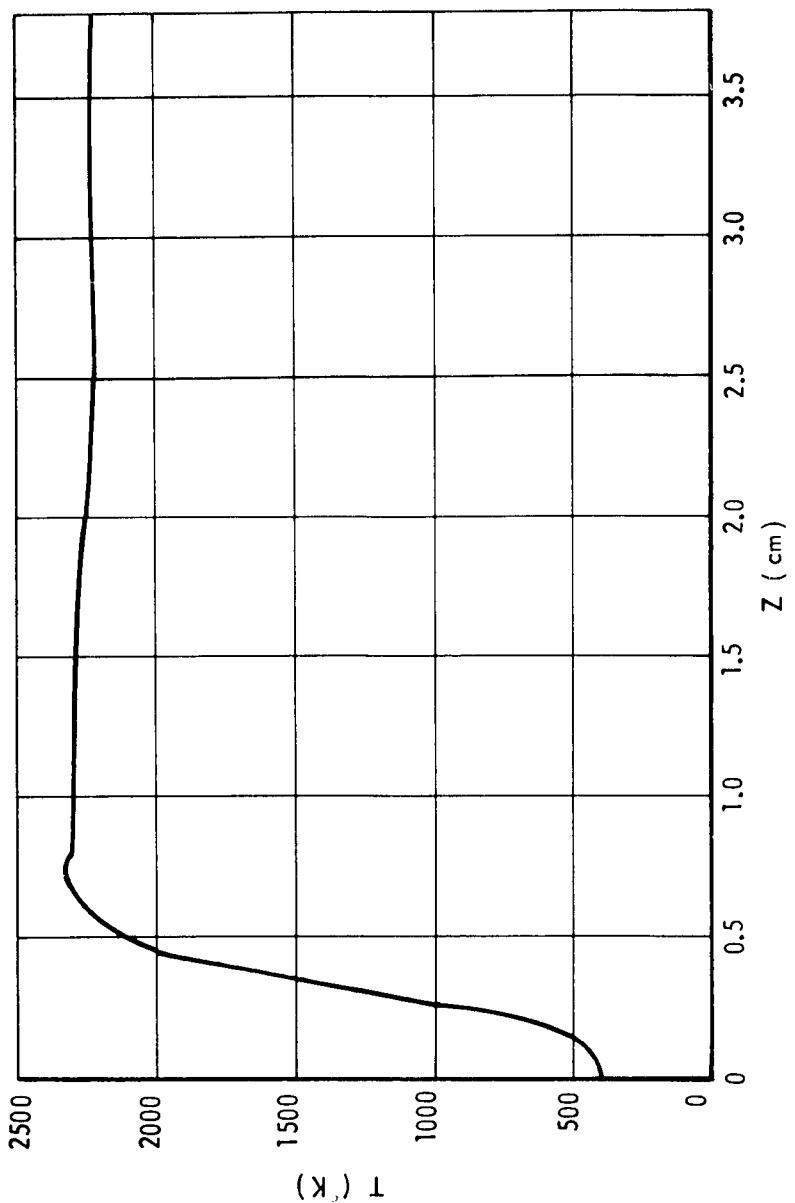


Fig. IV-1 TEMPERATURE PROFILE OF A SPHERICAL METHANE FLAME  
( $\text{CH}_4=0.09, \text{O}_2=0.18, \text{A}=0.728$ )  $P = 0.05 \text{ Atm}$ . TEMPERATURE ( $^{\circ}\text{K}$ )  
PLOTTED AGAINST DISTANCE THROUGH THE FLAME FRONT (cm.)

MEASUREMENT OF BINARY GASEOUS DIFFUSION  
COEFFICIENTS AT ELEVATED TEMPERATURES

G. Frazier, (A. A. Westenberg) and R. M. Fristrom

A point source apparatus for determining binary gaseous diffusion coefficients at atmospheric pressure was assembled and tested (Ref. 4, 5). Data were obtained for the system  $H_2$  (trace)-Ar covering the range up to 1000°K (Fig. IV-2). Higher temperatures were not attempted for fear of burning out the furnace.

Following these measurements materials were incorporated into the apparatus to allow corrosive gases to be used as trace components. In addition, the calibration constant was obtained for the system Argon-HBr (trace) to demonstrate that the thermal conductivity cell used for the analysis would be satisfactory for use with corrosive gases. This value was constant over the two day test duration. This test also indicated that the regulator used did not hold the HBr pressure constant. A search is therefore being made for a more precise pressure regulator.

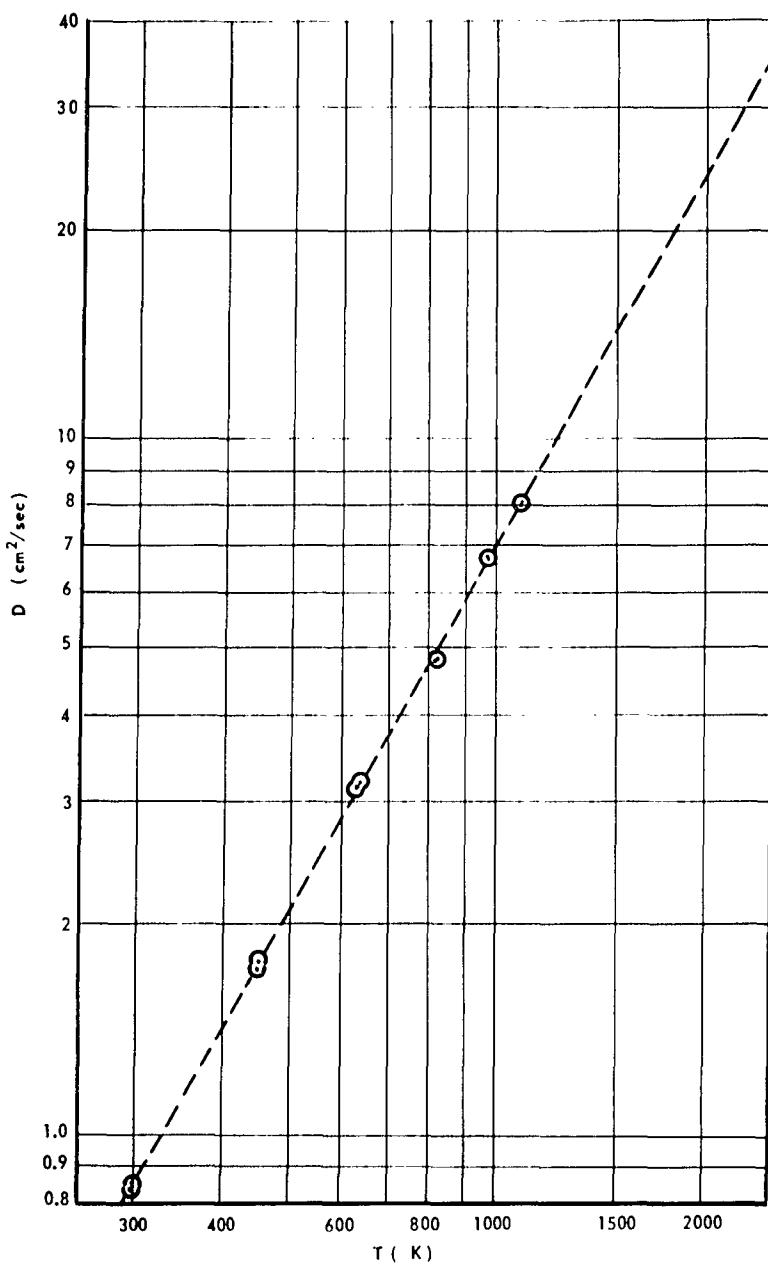


Fig. IV-2 DIFFUSION COEFFICIENT OF THE SYSTEM  $\text{H}_2$  (trace)-Ar AS A FUNCTION OF TEMPERATURE  $D$  ( $\text{cm}^2/\text{sec}$ )/(logarithmic scale) vs.  $T$  ( $^\circ\text{K}$ ).

## ANALYSIS OF FLAME STRUCTURE DATA

S. Favin and R. Fristrom

The flame structure data previously reported (Ref. 1) have been completed this quarter by the measurement of a temperature profile (see pp 9). This constitutes sufficient information for an analysis of the data if suitable diffusion coefficients can be provided. Only the Hydrogen-Argon system has been studied over a wide temperature range (see pp 12); but values of reasonable reliability can be estimated from available low temperature data and simple kinetic theory considerations (Ref. 6). A set of diffusion coefficients were recommended for the analysis of these flames.\* (Table IV-1). They are thought to be reliable to 20 percent and are of sufficient accuracy that a reasonable analysis is possible.

The information in which we seek is the fluxes of the various species and their net rates of reaction. The method of analysis employed is outlined in Appendix I. The data which are required are the compositions, temperatures, and diffusion coefficients for each species at each point in the flame. The original experimental data have been presented elsewhere in this report (pp 12) and in previous quarterly reports (Ref. 1). For purposes of analysis it is necessary to determine first and second derivatives of these data.

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\* We would like to thank Dr. A.A. Westenberg of APL for these recommendations.

Table IV-1  
 Binary Diffusion Coefficients of 0.05 atm  
 with Argon Carrier

TEMP	CO2	O2	CO	H2O	CH4	H2	H2CO
100.	0.43	0.61	0.61	0.73	0.64	2.49	0.44
200.	1.44	2.07	2.07	2.46	2.16	8.36	1.48
300.	2.92	4.20	4.20	5.00	4.40	17.00	3.00
400.	4.83	6.95	6.95	8.27	7.28	28.12	4.96
500.	7.14	10.27	10.27	12.22	10.76	41.56	7.33
600.	9.82	14.13	14.13	16.82	14.80	57.18	10.09
700.	12.86	18.50	18.50	22.03	19.38	74.89	13.22
800.	16.25	23.37	23.37	27.82	24.48	94.60	16.69
900.	19.97	28.72	28.72	34.19	30.09	116.25	20.52
1000.	24.01	34.54	34.54	41.12	36.18	139.79	24.67
1100.	28.37	40.81	40.81	48.58	42.75	165.17	29.15
1200.	33.04	47.52	47.52	56.57	49.76	192.33	33.94
1300.	38.00	54.66	54.66	65.07	57.27	221.25	39.04
1400.	43.27	62.23	62.23	74.09	65.20	251.89	44.45
1500.	48.82	70.22	70.22	83.59	73.56	284.21	50.16
1600.	54.66	78.61	78.61	93.59	82.36	318.20	56.15
1700.	60.77	87.41	87.41	104.06	91.57	353.81	62.44
1800.	67.17	96.61	96.61	115.01	101.21	391.03	69.01
1900.	73.83	106.20	106.20	126.42	111.25	429.84	75.85
2000.	80.76	116.17	116.17	138.30	121.70	470.21	82.98
2100.	87.96	126.52	126.52	150.62	132.55	512.12	90.57
2200.	95.42	137.25	137.25	163.40	143.79	555.55	98.04
2300.	103.14	148.36	148.36	176.62	155.42	600.50	105.97
2400.	111.12	159.83	159.83	190.27	167.44	646.93	114.16
2500.	119.35	171.67	171.67	204.36	179.84	694.83	122.62

Therefore, a machine program was used to smooth the data and provide the required derivatives (Ref. 1). A table of smooth values of the intensive properties and their derivatives were compiled at standard distance increments. Standard deviations of the experimental data from the smooth values were also determined. Using these data, fluxes of the various species were calculated. These flux data were examined for consistency and the rate data calculated by taking the spatial derivatives numerically using the previously described program.

The results of this analysis of the uninhibited flame were compiled and the rates for methane disappearance in the inhibited and uninhibited flames were compared (Fig. IV-3).

It is evident that a significant part of the reaction was occurring in the surface of the ball. This greatly complicates comparison between the inhibited and uninhibited systems, since the surface effects will differ due to the different burning velocities (this changes the surface temperature). We are not prepared at the present time to interpret heterogeneous reaction systems, although this may prove to be of considerable interest at a later date. Therefore, it was decided to postpone the complete analysis until the information from the study of DBr inhibition is available.

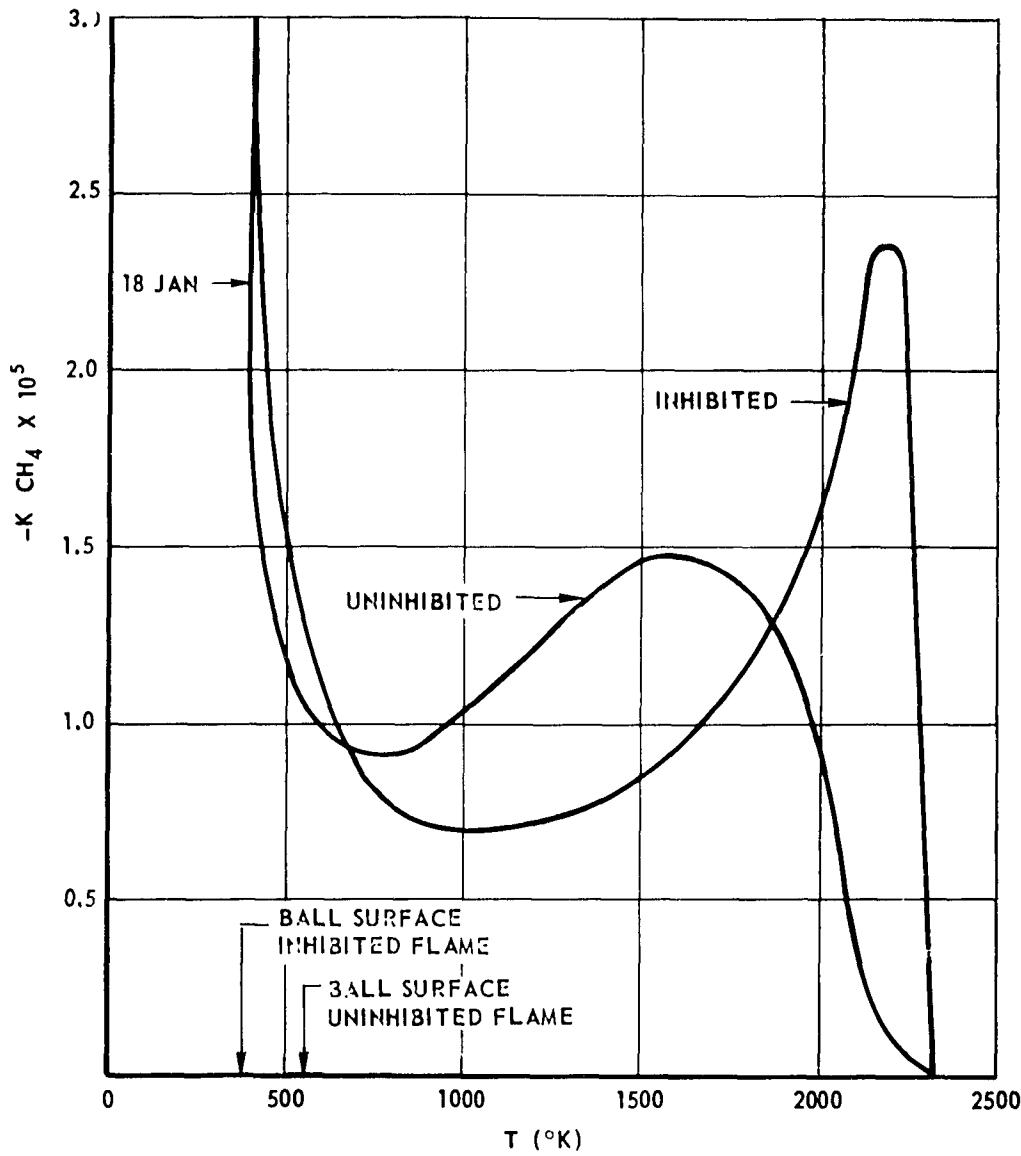


Fig. IV-3 RATE OF SPECIES APPEARANCE AND DISAPPEARANCE  
OF METHANE, OXYGEN WITH AND WITHOUT TRACES OF HBr.  
RATE OF REACTION (Moles/sec/cc) vs. TEMPERATURE  
( $^{\circ}$ K) AND SPECIES COMPOSITION (mole fraction).

The DBr and the new corrosion resistant burner are scheduled for completion during the next quarter. The new pump has sufficient pumping speed so that the surface reaction problem can be avoided. Since the DBr is quite expensive the new system will be tested using first the uninhibited flame and then the HBr inhibited flame and finally the DBr. Data will be taken during these runs to supplement the present information. The new data may provide sufficient information so that a separation can be made of the homogeneous and heterogeneous contributions in the present data. This might prove to be an interesting technique for studying surface reactions.

## APPENDIX

### The Analysis of Experimental Data on Laminar Flame Structure\*

A. A. Westenberg

#### The Basic One-Dimensional Flame Equations

For present purposes, a laminar flame is assumed to fulfill the following conditions: (i) it is a steady state system, so that all macroscopic variables at any point in the flame zone are independent of time, (ii) it is essentially a constant pressure system, so that the equation of motion may be ignored, as well as all other effects due to pressure gradients,<sup>7</sup> (iii) effects due to viscosity, radiation, and external forces are negligible, and (iv) the reciprocal thermal diffusion (Dufour) effect is neglected. With these restrictions the equations governing the behavior of a laminar flame may be written in general form as that of over-all continuity

$$\nabla \cdot (\rho \underline{v}) = 0, \quad (1)$$

of species continuity

$$\nabla \cdot \left[ N_i (v + v_i) \right] = k_i, \quad (2)$$

of energy conservation

$$\nabla \cdot \left[ \rho \hat{H}_v + \sum_i N_i H_i v_{-i} - \lambda \nabla T \right] = 0, \quad (3)$$

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\*This is an extract from Chapter 13 of a book, Flame Structure - Its Measurement and Interpretation, being prepared by R. M. Fristrom, A. A. Westenberg, and W. G. Berl.

where the specific enthalpy of the mixture  $\hat{H}$  is given in terms of the molar enthalpies  $H_i$  by  $\hat{H} = \frac{1}{\rho} \sum_i N_i H_i$ , and the equation of state  $P = \rho RT$ . (4)

In addition, the diffusion velocity is given by

$$v_i = \frac{N^2}{N_i \rho} \sum_j M_j D_{ij}^* \nabla \left( \frac{N_j}{N} \right) - \frac{D_i^* T}{N_i M_i} \nabla \ln T \quad (5)$$

Now in this analysis we shall be interested in one-dimensional forms of the basic equations (1), (2), (3) and (5), since it is only in this form that experimental flame structure data may be conveniently handled. The so-called "flat" flames are not strictly one-dimensional in the sense that changes in the macroscopic variables occur only along a distance coordinate  $z$  normal to the direction of flame propagation. In real flat flames there is lateral expansion of the gas parallel to the direction of propagation in varying degree as it traverses the reaction zone, so that strictly speaking, one cannot refer to the flame as one-dimensional at all. Hence it is necessary to invoke the concept of a pseudo one-dimensional flame in analogy to the treatment of fluid flow in a pipe of varying cross section. The actual quantity - for example, the  $z$ -component of gas velocity - which varies to some extent across the streamtube, is replaced by an averaged quantity over the streamtube area which is constant. As long as the rate of change of the quantity in the  $z$ -direction is much larger than that at right angles this is a valid procedure, and this will always be the case in the flames of interest here.

The continuity equation may be written

$$\rho v A = \text{constant.} \quad (6)$$

In other words, the averaging is done so that Eq. (6) is satisfied at any  $z$ , or this equation defines the averaging process. In this way we have derived the familiar one-dimensional over-all continuity equation for flow of varying area. If the subscript "o" denotes some reference point, as for example, the cold boundary of a flat flame, Eq. (6) may be written as

$$\begin{aligned} \rho v A &= \rho_o v_o A_o && \text{or} \\ \rho v A &= \rho_o v_o \end{aligned} \quad (7)$$

where  $A = a/a_o$  is the streamtube area ratio at any point.

In a similar manner, the other equations may be reduced to one-dimensional form suitable for flat flames with lateral expansion. Thus the species continuity equation (2) becomes

$$\frac{d}{dz} \left[ N_i (v + v_i) A \right] = K_i A \quad (8)$$

and the energy equation (3) becomes (after integration with respect to  $z$ )

$$\rho_o v_o \hat{H} + A \sum_i N_i H_i v_i - A \lambda \frac{dT}{dz} = \text{constant.} \quad (9)$$

If it may be assumed that the transport terms (the second and third terms on the left) vanish at the cold boundary, the integration constant

may be set equal to  $\rho_o v_o \hat{H}_o$ . This condition may not always be fulfilled in practical flames. However, the transport terms always vanish at the hot boundary - denoted by the subscript " $\infty$ " - so the integration constant may always be equated to  $\rho_o v_o \hat{H}_{\infty}$ . If the transport terms also vanish at the cold boundary, then  $H_o = H_{\infty}$ , of course. Equations (7), (8), (9), and one-dimensional diffusion velocity expression

$$v_i = \frac{N^2}{N_f \rho} \sum_j M_j D_{ij}^* \frac{d}{dz} \left( \frac{N_j}{N} \right) - \frac{D_i^T}{N_f M_i} \frac{d \ln T}{dz} \quad (10)$$

are the basic equations of change for plane flames realized in the laboratory. The idealized, truly one-dimensional plane flames widely used in theoretical work may be easily obtained from them by setting  $A = 1$ .

In the case of a flame with spherically symmetric geometry the problem is simpler, since these are truly one-dimensional systems attainable in practice. If  $r$  is the radial distance coordinate, the flame equations take the form of over-all continuity

$$m_s = 4\pi r^2 \rho v = 4\pi r_o^2 \rho_o v_o , \quad (11)$$

where  $m_s$  is the (constant) total mass flow rate through the flame, species continuity

$$\frac{d}{dr} \left[ r^2 N_i (v + v_i) \right] = r^2 K_i , \quad (12)$$

energy conservation

$$r^2 \left[ \hat{\rho} H v + \sum_i N_i H_i v_i - \lambda \frac{dT}{dr} \right] = \text{constant} , \quad (13)$$

and the radial diffusion velocity

$$v_i = \frac{N^2}{N_i \rho} \sum_j M_j D_{ij}^* \frac{d}{dr} \left( \frac{N_j}{N} \right) - \frac{D_i^T}{N_i M_i} \frac{d \ln T}{dr}. \quad (14)$$

In these equations  $v$  is now the radial mass average velocity component.

It is convenient in the analysis of flame structure data to make use of an additional variable in some cases. This is the species mass flux fraction  $G_i$  defined by

$$G_i = \frac{N_i M_i (v + v_i)}{\rho v}. \quad (15)$$

It represents the fraction of the total mass flux per unit area which is due to species  $i$ , and includes the contribution due to diffusion as well as convection. Thus if the concentration of  $i$  decreases downstream (i.e. in the direction of positive  $z$  or  $r$ ), the species will have a positive  $v_i$ , and to a stationary observer the species will contribute a greater fraction of the total mass flux than would be predicted on the basis of its concentration and simple mass flow (convection) alone. Conversely, a species increasing in concentration downstream will have a negative  $v_i$  (diffuse upstream) and this will reduce its contribution to the total flux. By definition of the diffusion velocity,  $\sum_i N_i M_i v_i = 0$ , and from Eq. (15) we have  $\sum_i G_i = 1$  (since  $\sum_i N_i M_i = \rho$ ) as required of a fractional variable. Using the  $G_i$  variable, the basic one-dimensional flame equations may be summarized in compact form. For the plane flame, these are

$$\frac{\rho_o v_o}{M_i} \frac{dG_i}{dz} = k_i A , \quad (16)$$

$$\rho_o v_o \sum_i \frac{H_i G_i}{M_i} - A \lambda \frac{dT}{dz} = \rho_o v_o \hat{H}_\infty \quad (17)$$

in addition to Eqs. (7), (10), and (14).

For the spherical flame, we have

$$\frac{m_s}{4\pi M_i} \frac{dG_i}{dr} = r^2 k_i , \quad (18)$$

$$\sum_i \frac{H_i G_i}{M_i} - \frac{4\pi r^2 \lambda}{m_s} \frac{dT}{dr} = \hat{H}_\infty \quad (19)$$

in addition to Eqs. (11), (14), and (15).

#### Obtaining the Diffusion Velocities

The first step in the application of the flame equations to a set of experimental data is the computation of the diffusion velocities  $v_i$  for all species for which concentration profiles are available. The rigorous expression for this quantity is given by Eq. (10) and involves the complex multicomponent diffusion coefficients  $D_{ij}^*$ . The rigorous expression is rarely, if ever, used in practice.

Instead the usual flame data are obtained in a system where one component  $j$  is a diluent present in large excess so that the other components  $i$  may be treated as a trace in a binary mixture with  $j$ . In that case, the diffusion velocity is given in good approximation by the simple

relations

$$\text{Plane: } V_i = - \frac{N D_{ij}}{N_j} \frac{d}{dz} \left( \frac{N_j}{N} \right) = - \frac{D_{ij}}{X_j} \frac{dX_j}{dz} \quad (20)$$

$$\text{Spherical: } V_i = - \frac{N D_{ij}}{N_j} \frac{d}{dr} \left( \frac{N_j}{N} \right) = - \frac{D_{ij}}{X_j} \frac{dX_j}{dr} \quad (21)$$

for the two geometries, in which thermal diffusion has been neglected.

This is by far the most common procedure. The gradients  $dX_j/dz$  or  $dX_j/dr$  are determined for each species at convenient intervals throughout the flame zone directly from the experimental concentration profiles.

Numerical differentiation of the smoothed profiles generally is adequate over most of the curves, but where they are changing slope rapidly and in the region of concentration maxima, it is sometimes necessary to use graphical differentiation.

It should be noted that Eq. (20) is not valid for the diffusion velocity of an excess component. Since, by definition, a component present in excess is presumed to be negligibly consumed by reaction, its concentration will be relatively constant through the flame zone, and hence its diffusion velocity may be neglected.

After the  $V_i$  profiles are determined in this way, profiles of  $G_i$  are easily computed according to Eq. (15). (For the excess species,  $G_i$  may be taken to be the mass fraction  $N_i M_i / \rho_0$ .) The computed  $G_i$  should then be checked against the requirement that  $\sum_i G_i = 1$ .

### Derivation of Net Reaction Rates

Perhaps the most important and useful type of information to be obtained from laminar flame structure analyses is the net reaction rate for each species throughout the flame zone. These are the quantities  $K_i$ , the net rate of appearance or disappearance per unit volume having the common unit of moles  $\text{cm}^{-3} \text{sec}^{-1}$ . From Eqs. (16) and (18) we obtain directly

$$K_i = \frac{\rho_o v_o}{M_i A} \frac{dG_i}{dz} \quad (\text{plane}) \quad (23)$$

$$K_i = \frac{m_s}{4\pi r^2 M_i} \frac{dG_i}{dr} \quad (\text{sphere}) \quad (24)$$

so that the desired rate profiles may be computed by numerical differentiation of the flux profiles  $G_i$ . It is convenient to check the computed rates by noting that, as previously pointed out, for any element

$$\sum_i v_i K_i = 0 \quad (25)$$

by conservation of matter. Thus the calculated rates should fulfill the condition expressed by Eq. (25) for each element present.

Since the determination of the quantities  $G_i$  involves a differentiation of the composition data in finding the diffusion velocities which contribute to the  $G_i$ , it will be apparent from Eqs. (23) and (24) that the reaction rates  $K_i$  obtained from the flame necessarily involve second derivatives of experimental data.

This is an unfortunate but unavoidable source of error, and makes it clear why highly refined sampling and chemical analysis techniques are required in order to get meaningful results. It also strongly points out the need for reliable diffusion coefficients, which enter into the determination of the  $G_i$ , and hence  $K_i$ .

#### Heat Release Rates

Of general interest in any laminar flame analysis is the determination of the rate of heat release per unit volume throughout the flame zone. There are two independent ways of doing this from a given set of data. Perhaps the simplest and most obvious approach is to use the net reaction rates  $K_i$  and the absolute molar enthalpies  $H_i^8$  in the relation

$$Q = - \sum_i H_i K_i \quad (26)$$

where  $Q$  is the volumetric heat release rate, and the negative sign means that (opposite to the usual thermodynamic convention) heat evolved is positive. (No case has ever been found where heat was absorbed anywhere in a flame, nor is it likely that there is any such flame.) The alternative method is to combine the energy and species continuity equations. Thus for the plane flame Eq. (17) may be written

$$\frac{d}{dz} \left\{ \rho_o v_o \sum_i \frac{H_i G_i}{M_i} - A\lambda \frac{dT}{dz} \right\} = 0, \quad \text{or}$$

$$\rho_o v_o \left[ \sum_i \frac{H_i}{M_i} \frac{dG_i}{dz} + \sum_i \frac{G_i}{M_i} \frac{dH_i}{dz} \right] - \frac{d}{dz} \left[ A\lambda \frac{dT}{dz} \right] = 0.$$

But by definition of the molar heat capacity at constant pressure

$$\frac{dH_i}{dz} = \frac{dH_i}{dT} \frac{dT}{dz} = (C_p)_i \frac{dT}{dz},$$

and using this with Eq. (16) in the previous relation gives

$$A \sum_i H_i K_i + \rho_o v_o \frac{dT}{dz} \sum_i \frac{G_i (C_p)_i}{M_i} - \frac{d}{dz} \left[ A\lambda \frac{dT}{dz} \right] = 0,$$

or, in view of Eq. (26),

$$Q = \frac{1}{A} \left\{ \rho_o v_o \frac{dT}{dz} \sum_i \frac{G_i (C_p)_i}{M_i} - \frac{d}{dz} \left[ A\lambda \frac{dT}{dz} \right] \right\}. \quad (27)$$

The method of computing  $Q$  from Eq. (26) involves only the net chemical rates and enthalpies, so it is a direct measure of the rate of enthalpy change per unit volume due to reaction. In Eq. (27),  $Q$  is regarded as a source term in the enthalpy flux conservation equation and involves directly the  $G_i$  and a second derivative of the temperature profile. Ideally, of course, both methods should give the same result, and the degree to which they do in a real example is a useful check on the data and their analysis.

For the spherical flame, Eq. (26) still applies, of course, while the other relation may be shown to be

$$Q = \frac{m_s}{4\pi r^2} \left\{ \frac{dT}{dr} \sum_i \frac{G_i (C_p)_i}{M_i} - \frac{d}{dr} \left[ \frac{4\pi r^2 \lambda}{m_s} \frac{dT}{dr} \right] \right\} \quad (28)$$

It may be noted that a heat release rate profile computed from a measured temperature profile by means of Eq. (28) has sometimes been used to make inferences regarding net reaction rates<sup>9,10</sup> especially when composition profiles have not been measured and combined with appropriate diffusion data to give flux profiles, and then  $K_i$  values directly. In these cases, it is the practice to replace the term  $\sum_i G_i (C_p)_i / M_i$  in Eq. (27) by an "average" heat capacity - generally taken to be that of the major component, if any. A Q profile is then calculated, and if it can be assumed that only one (known) chemical reaction contributes the major portion of the heat release, the  $K_i$  profiles for reactant and product can be obtained from Eq. (26). The shortcomings of this procedure are obvious for all but the simplest flames.

Another calculation of some importance is the integrated heat release rate profile, i.e. the total heat release rate in a stream tube of unit initial area up to any point z in the plane flame. This is given by the integral

$$\int_0^z Q A dz$$

which may be obtained by numerical (graphical) integration of the QA profile. For the spherical flame, the total heat release rate in the spherical volume of radius r is given by

$$4\pi \int_{r_o}^r Q r^2 dr .$$

As Friedman and Burke have pointed out <sup>11</sup>, the value of the integrated heat release at the hot boundary should be given by

$$\int_0^{\infty} Q A dz = \rho_o v_o (\Delta H_c)_o \quad (29)$$

where  $(\Delta H_c)_o$  is the heat of combustion per unit mass of unburned mixture. This must be so, since from Eq. (27)

$$\int_0^{\infty} Q A dz = \rho_o v_o \int_0^{\infty} \sum_i \frac{G_i (C_p)_i}{M_i} dT - \int_0^{\infty} d \left[ A \lambda \frac{dT}{dz} \right].$$

The second integral vanishes because  $dT/dz = 0$  at  $z = 0$  and  $z = \infty$ , and the first integral is simply the heat of combustion at the cold gas temperature. Eq. (29) may be used only as a check on the internal consistency of the computed heat release profiles. It proves nothing about the accuracy of the experimental data, however.

3/15/60  
AAW/ccl  
11/17/61  
AAW/cec

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TG 376-4  
NOVEMBER 1961

# FLAME INHIBITION RESEARCH

YEARLY SUMMARY  
1 November, 1960 - 31 October, 1961

THE JOHNS HOPKINS UNIVERSITY  
**APPLIED PHYSICS LABORATORY**  
8621 GEORGIA AVENUE                    SILVER SPRING, MARYLAND

Summary of Accomplishments for the Year  
1 November 1960 - 31 October 1961

1. The structures of stoichoimetric and oxygen rich methane flames have been studied with and without traces of a sample inhibitor (HBr).
2. The data for the stoichoimetric (spherical) flame have been partially analyzed. The rates of methane disappearance have been calculated. It was found in both the inhibited and uninhibited flame that a significant part of the reaction was occurring on the surface of this sphere.
3. A new technique for studying radical and atom concentrations in flames has been studied. The method combines microprobe sampling with chemical scavenging. It was qualitatively successful in the study of hydrogen atoms and quantitatively successful in the study of oxygen atoms.
4. The diffusion coefficient of A-H<sub>2</sub> (trace) has been measured between 295°K and 1079°K
5. A computer program has been developed to aid in the analysis of flame structure data.
6. A set of calculations have been made of the adiabatic flame temperatures and compositions of some representative methane oxygen flames with and without the added HBr. These calculations showed the effect of HBr on the radical concentrations in the burned gases.

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# FLAME INHIBITION RESEARCH

## III. SUMMARY OF PREVIOUS WORK

### SUMMARY OF WORK PRIOR TO 1 NOV. 1960

The work prior to the initiation of this contract (on 1 November 1960) consisted of a survey of the possibilities of applying flame structure data to flame inhibition studies, and a suggested program for such studies. This work was summarized in a proposal submitted to the U. S. Army Engineering Research and Development Laboratory in October 1960 (Ref. 4, on page 2).

### SUMMARY OF PROGRESS, 1 NOV. 1960 - 31 JAN. 1961

(1) A flat flame burner was set up for flame inhibition studies. The previously studied methane and oxygen flame ( $\text{CH}_4$  - 0.078,  $\text{O}_2$  - 0.92; pressure 0.05 atm) was successfully stabilized with added inhibitor (HBr) up to concentrations of 0.0035 mole fraction.

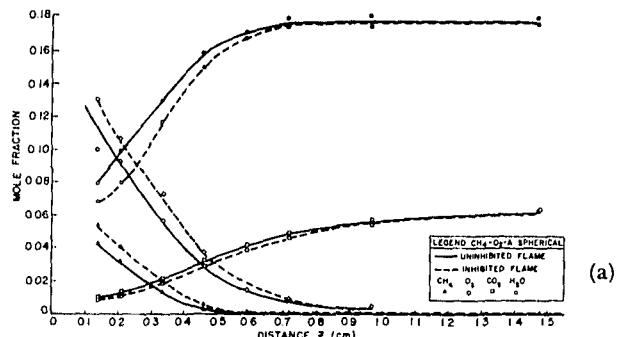
(2) Using the uninhibited flame, two flame composition profiles were run on the new time-of-flight mass spectrometer. A third run was made on an inhibited flame to test the sensitivity of the instrument for HBr. From these test runs it was concluded that the instrument requires the addition of a trap current regulator to allow quantitative work and a forepump trap to shorten the HBr pump-out time. These items have been ordered, and the inhibitor studies have been temporarily transferred to the CEC magnetic-deflection spectrometer.

(3) A computing machine routine for the automatic reduction of flame structure data has been developed.

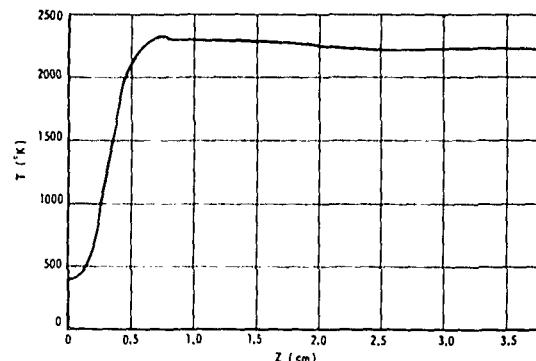
(4) A report on the flame inhibition program was presented 15 November 1960 at the meeting on "Inhibition of Ignition and Flames with Chemicals." This meeting was sponsored by the Committee on Fire Research of the National Academy of Sciences, National Research Council.

### SUMMARY OF PROGRESS, 1 FEB. - 30 APR. 1961

(1) A spherical flame apparatus was set up for inhibition studies on the system ( $\text{CH}_4$  - 0.09,  $\text{O}_2$  - 0.179, Ar - 0.727, pressure 0.05 atm). Composition profiles were measured for both the inhibited and uninhibited flames with the same total mass flow. In addition to measuring the concentrations of the species which were stable to sampling, an attempt was made to measure hydrogen-atom concentration profiles using a new device, "the scavenger sampling probe." Qual-



(a)



(b)

Figure III-1 THE EFFECT OF ADDED HBr ON THE CHARACTERISTIC PROFILES OF A STOICHIOMETRIC METHANE FLAME. COMPOSITION OF THE MAJOR SPECIES (mole fractions) AND TEMPERATURE IS PLOTTED AGAINST DISTANCE, Z (cm.).

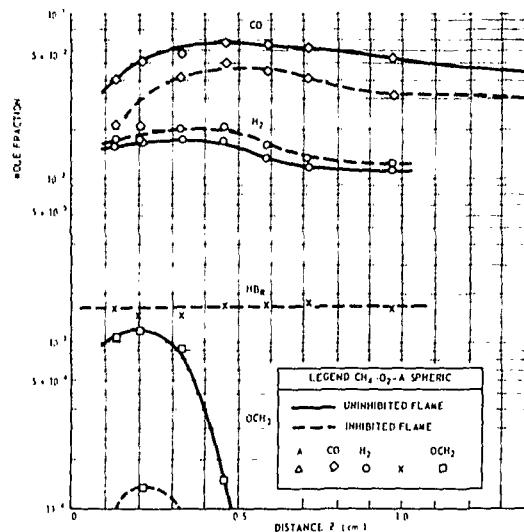


Figure III-2 THE EFFECT OF ADDED HBr ON THE CONCENTRATIONS OF INTERMEDIATE SPECIES IN A STOICHIOMETRIC METHANE FLAME.

itative consideration of these results yields the following information:

- (a) The addition of this amount of inhibitor ( $X(HBr) = 0.0015$ ) appreciably lowers the rate of reaction of the major species ( $CH_4$ ,  $O_2$ , and  $CO$ ).
- (b) Peak concentrations of the intermediate species ( $OCH_2$ ,  $CO$ , and  $H_2$ ) are changed and shifted relative to the major species. When data on diffusion and temperature become available, a quantitative interpretation may yield  $H$ ,  $OH$ , and  $CH_3$  radical concentration data.
- (c) The apparent concentration of  $H$  atoms was depressed almost five-fold by the addition of  $HBr$  even in the equilibrium region.
- (d)  $HBr$  was the only bromine-containing compound detected ( $X(Br_2) < 10^{-4}$ ).

These latter two results are probably artifacts of the techniques. They may, however, yield useful information and provide a guide for subsequent work.

(2) A series of computer calculations were made of the adiabatic temperatures and compositions of the equilibrium burned gases of some  $CH_4$  -  $O_2$  - Ar mixtures and of the effect of adding small amounts of  $HBr$ . A routine developed by the U. S. Naval Ordnance Test Station was used on the APL computer to determine these flame properties. One of the most interesting points developed was that the  $HBr$  is almost completely dissociated and that bromine atoms are the commonest inhibitor species in the burned gases.

#### SUMMARY OF PROGRESS, 1 MAY 31 JULY 1961

(1) A set of composition and temperature profiles was determined for a flat methane-oxygen flame ( $CH_4$  - 0.078,  $O_2$  - 0.02,  $P$  = 0.05 atm) with and without added  $HBr$ . Corrosion was so severe that the burner assembly became unusable. A new teflon-glass-ceramic system including traps to protect the pumps has been designed and is being fabricated.

(2) A program to measure the high-temperature diffusion coefficients for the analysis of the inhibited flames has been started. The apparatus has been activated and tested at 300°K and 500°K on the well-known  $He-N_2$  system. Measurements have been started on the  $Ar-H_2$  system.

(3) Scavenger probe studies of radical concentrations in flames have been continued. The use of chlorinated hydrocarbons as scavenger for  $H$  atoms has been shown to be proportional to  $H$ , but the scavenging efficiency was found to be only 10%. Studies of oxygen-atom concentration using  $NO_2$  as a scavenger have been made.

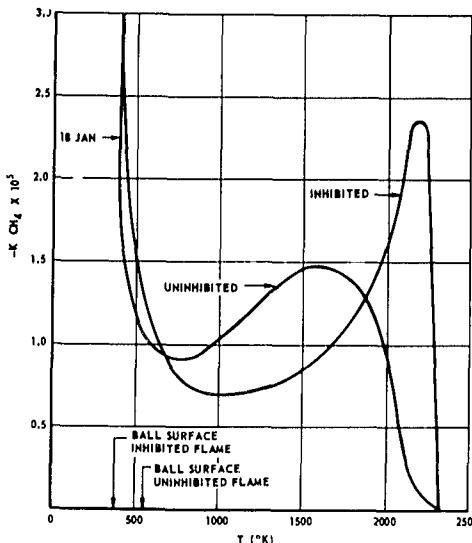


Figure III-3 THE EFFECT OF  $HBr$  ON THE RATE OF METHANE DISAPPEARANCE IN A STOICHIOMETRIC FLAME ( $CH_4$  - 0.09  $O_2$  0.179 A-0.727;  $P$  = 0.05 Atm.).  $K_{CH_4}$  (MOLES PER CUBIC cm. per sec  $\times 10^5$ ) VERSUS TEMPERATURE (°K).

NOTE THAT AN APRECIABLE PART OF THE REACTION APPEARS TO BE OCCURRING AT OR NEAR THE SURFACE OF THE BALL. THE PRINCIPAL EFFECT OF THE ADDED  $HBr$  APPEARS TO BE A SHIFT OF THE REACTION TO THE HIGH TEMPERATURE REGION.

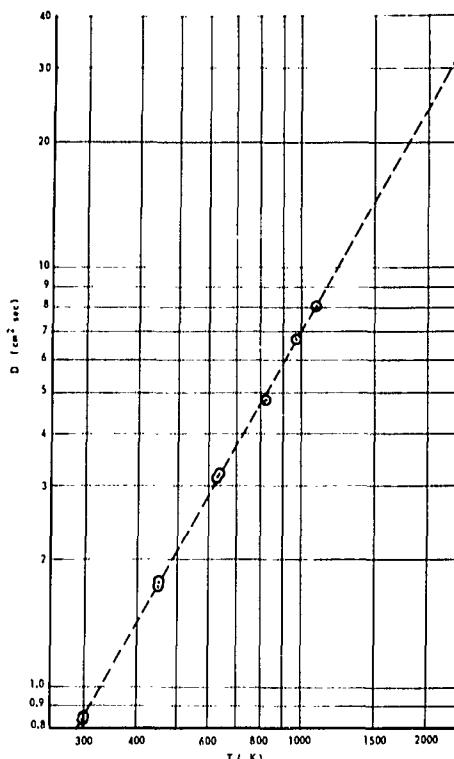


Figure III-4 DIFFUSION COEFFICIENT OF THE SYSTEM  $H_2$  (trace) - Ar AS A FUNCTION OF TEMPERATURE

The efficiency of scavenging appears to be high and may approach 100%.

SUMMARY OF PROGRESS 1 AUG. - 31 OCT. 1961

(1) A temperature profile was measured on the spherical stoichiometric methane-oxygen-argon flame system whose composition structure was reported in TG 331-2. (See pp 9)

(2) The diffusion coefficient of the system A-H<sub>2</sub> (tract) was measured at atmospheric pressure over the range 300 - 1070°K. (See pp 12)

(3) An analysis was made of the effect of added HBr on the fluxes and rates on the stoichiometric methane flame. (See pp 14). This indicated that a significant fraction of the reaction occurred on the surface of the ball.

Table III-1  
Test of Oxygen-Atom Scavenger Probe\*

System		O <sub>2</sub>	Ar	T <sub>0</sub> (K)	P (atm)	Expt'l.	Calculated**
CH <sub>4</sub>	0.078	0.02	0.002	313	4.1	0.0019	0.0020
	0.10	0.18	0.72	313	3.8	0.0030	0.00325

\* Using the reaction O + NO<sub>2</sub> + NO → O<sub>2</sub> for scavenging in flame interprobe-sampling studies (see Figure III-5a below), the O-atom concentrations were found in the equilibrium burned gas region.

\*\* Values interpolated from calculation made using T<sub>0</sub> = 400°K.

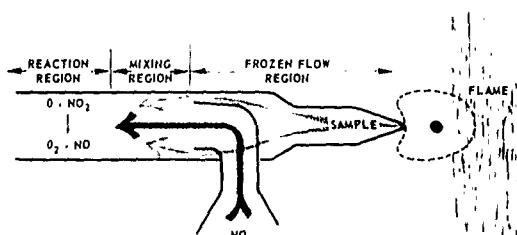


Figure III-5a SCHEMATIC DIAGRAM OF SCAVENGER PROBE USED IN MEASURING OXYGEN-ATOM CONCENTRATIONS

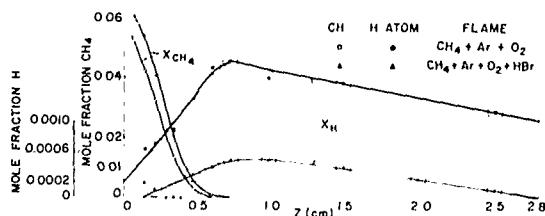


Figure III-5b EFFECT OF ADDED HBr ON COMPOSITION PROFILES OF METHANE AND HYDROGEN ATOMS IN A METHANE FLAME

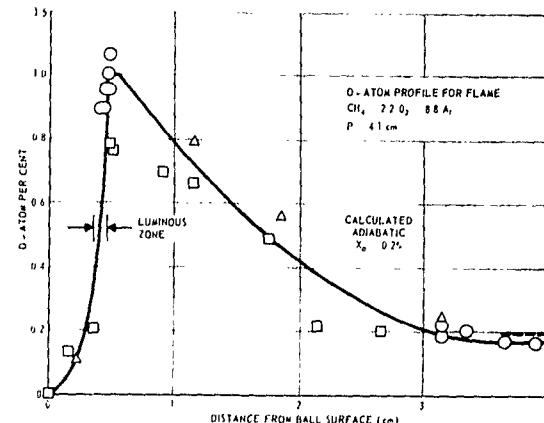


Figure III-5c TEST OF OXYGEN-ATOM SCAVENGER PROBE

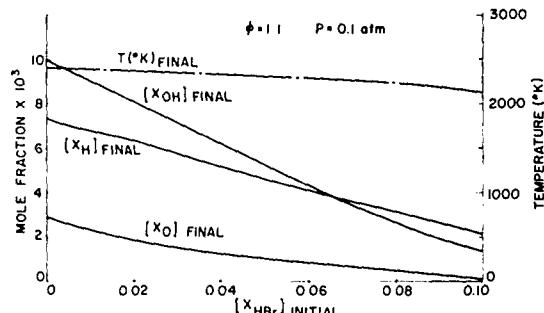


Figure III-6a EFFECT OF ADDED HBr ON FLAME RADICAL CONCENTRATIONS (H, O, OH)

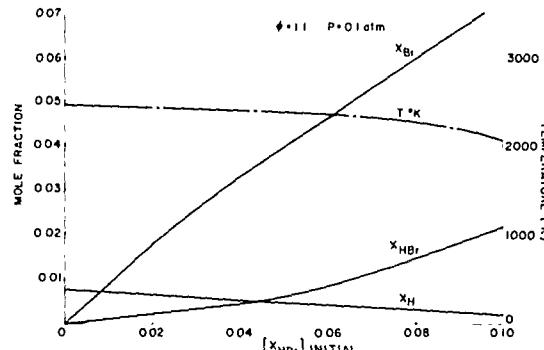


Figure III-6b EFFECT OF HBr CONCENTRATION ON INHIBITOR SPECIES CONCENTRATIONS (HBr, Br, Br<sub>2</sub>)

## FLAME INHIBITION STUDIES

### YEARLY SUMMARY (1 November 1960 - 31 October 1961)

The objective of the first year of flame inhibition studies was to develop techniques and obtain a preliminary understanding of processes involving flame inhibition by measuring and analyzing the structure of flames with and without the addition of simple halogen containing compounds.

The methane-oxygen flame was chosen for study because of previous experience with this system and because it offered a compromise between chemical simplicity and systems of practical interest.

A stoichoimetric flame and an oxygen diluted flame were studied using previously developed flame structure techniques for making temperature and composition measurements. Supplemental studies were made of high temperature diffusion coefficients appropriate to these systems. An effort was made to develop a technique for determining the concentrations of free radicals and atoms in flames by combining probe sampling and chemical scavenging. In addition, machine techniques for reducing flame structure data were developed and calculations of adiabatic flame temperatures and compositions were made for a representative set of inhibited (and uninhibited flames) with a view to determining the effect of added HBr on equilibrium radical concentrations.

This work is outlined in the collected Quarterly Progress Summaries and the most important contributions are listed in the Yearly Summary of Accomplishments.

#### PRESENT STATUS OF FLAME INHIBITION PROJECT

During the past year a number of significant pieces of information have been developed at this Laboratory and other combustion research centers so that it appears that a feasible goal for the coming year will be to collect sufficient information on the systems associated with HBr inhibited methane flames to allow the proposing and testing of a simplified theory of flame inhibition. The present status of this information is summarized in the following figure which shows how the available information fits into our overall plan for flame inhibition study. This information is quite extensive and it is particularly gratifying that several other laboratories are actively pursuing flame structure studies which compliment our work. Thus, for example, we feel that it will not be necessary for us to make further studies of the hydrogen oxygen, hydrogen bromine, or carbon monoxide oxygen flame systems, because these systems have either been studied or are presently being studied elsewhere. We informally exchange information with most of these laboratories and are following their work with interest.

The results of our own flame structure studies were somewhat disappointing since they showed the presence of a significant surface reaction. This complication makes the interpretation of the data impractical without the auxiliary information which is being gathered.

This difficulty may eventually become an advantage since it offers the possibility of the study of the inhibition of surface catalyzed combustion.

The high temperature diffusion coefficient measurements on the hydrogen-argon system were made as part of the program to fill in the gaps in such information on the systems of interest. The data was of high precision and appeared normal. Further studies are projected on HBr, Br<sub>2</sub>, and certain other species in an Argon carrier.

The study of radical concentrations using the scavenger probe technique were disappointing with respect to hydrogen atom, where it was found that scavenging with chlorinated hydrocarbons gave results which were proportional to hydrogen atom concentration, but quantitatively too low. In the case of oxygen atoms the NO<sub>2</sub> scavenger appeared to give good quantitative results. Further studies are underway.

The machine program (IBM 7090) for the analysis of flame structure data is satisfactory, but at present a number of hand operations and human decisions are still required. Efforts will be made to reduce the necessary amount of hand work.

The machine work for calculating adiabatic flame temperatures and compositions has proven very satisfactory. Further calculations are planned as they prove necessary.

STATUS OF FLAME STRUCTURE-INHIBITION AVAILABLE INFORMATION 1 NOV 1961

FLAME SYSTEM RADICAL INHIBITOR ↓ REACTIONS	H <sub>2</sub> - O <sub>2</sub>		CO - O <sub>2</sub>		CH <sub>4</sub> - O <sub>2</sub>		
	Profiles	1, 2, 3, 6 <th>Profiles</th> <td>1, 2, 3, 4<th>Profiles</th><td>1, 2, 3, 4, 5</td></td>	Profiles	1, 2, 3, 4 <th>Profiles</th> <td>1, 2, 3, 4, 5</td>	Profiles	1, 2, 3, 4, 5	
	Transport		Trans.	<th>Trans.</th> <td>8</td>	Trans.	8	
	Radicals	4, 5, 6, 7, 8, 9, 10	Rad.	5	Rad.	6, 7	
	Analysis	2	Anal.	1, 2, 3, 4	Anal.	2, 3, 4, 9	
	Interpretation	2	Inter.	1, 2, 3, 4	Inter.	2, 3, 4, 10, 11	
H Br		H <sub>2</sub> - O <sub>2</sub> - HBr		CO - O <sub>2</sub> - HBr		CH <sub>4</sub> - O <sub>2</sub> - HBr	
H + HBr ≠ H <sub>2</sub> + Br	1	Profiles		Profiles		Profiles	1, 2, 3
_____	_____	Trans.		Trans.		Trans.	4
_____	_____	Rad.		Rad.		Rad.	5
_____	_____	Anal.		Anal.		Anal.	6
_____	_____	Inter.		Inter.		Inter.	

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$\text{CH}_4 - \text{O}_2 - \text{HBr}$

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## ABSTRACT CARDS FOR FLAME INHIBITION STUDIES

TG 376-1

The Johns Hopkins University  
Applied Physics Laboratory  
Silver Spring, Maryland

FLAME INHIBITION RESEARCH PROGRESS REPORT, 1 November 1960 - 31 January 1961.

(1) A flat flame burner was set up for flame inhibition studies. The previously studied methane flame ( $\text{CH}_4 - 0.78\text{O}_2 - 0.92; \bar{P} = 0.05 \text{ atm}$ ) was successfully stabilized with added inhibitor ( $\text{HBr}$ ) up to concentrations of 0.0035 mole fraction.

(2) Using the uninhibited flame, two flame composition profiles were run on the new instrument. A light mass spectrometer, third run on an inhibited flame to test the sensitivity of the instrument for  $\text{HBr}$ . From these test runs it was concluded that the instrument requires the addition of a TRAP regulator to allow quantitative work and forepump trap to shorten the FIR pump-out time. These items have been ordered and the inhibitor studies have been temporarily transferred to the C magnetic deflection spectrometer.

(3) A computing machine routine for the automatic reduction of flame structure data has been developed.

(4) A report on the flame inhibition program was presented 15 November 1960 at the meeting on "Inhibition of Ignition and Places with Chemicals". This meeting was sponsored by the Committee on Fire Research of the National Academy of Sciences, National Research Council.

The Johns Hopkins University  
Applied Physics Laboratory  
Silver Spring, Maryland

FLAME INHIBITION R.S. AGC QUARTERLY PROGRESS REPORT,  
15 October 1960 - 31 October 1961.

(1) A spherical flame apparatus was set up for inhibition studies on the system ( $\text{CH}_4 - 0.9, \text{O}_2 - 0.179, \text{Ar} - 0.727$ , pressure 0.05 atm). Composition profiles were measured for both the inhibited and uninhibited flames with the same total mass flow. In addition to measuring the concentrations of the species which were stable to sampling, an attempt was made to measure hydrogen-concentration concentration profiles using a new device, the scavenger sampling probe. Qualitative consideration of these results yields the following information:

(a) The addition of this amount of inhibitor ( $X(\text{HBr}) = 0.0015$ ) appreciably lowers the rate of reaction of the major species ( $\text{CH}_4, \text{O}_2$ , and  $\text{CO}$ ).

(b) Peak concentrations of the intermediate species ( $\text{OCH}_3, \text{CO}_2$ , and  $\text{H}_2$ ) are changed and shifted relative to the major species. When data on diffusion and temperature become available, a quantitative interpretation may yield  $\text{H}_2$ ,  $\text{OH}$ , and  $\text{CH}_3$  radical concentration data.

(c) The apparent concentration of  $\text{H}$  atoms was depressed almost five-fold by the addition of  $\text{HBr}$  even in the equilibrium region.

(d)  $\text{HBr}$  was the only bromine containing compound detected ( $X(\text{Br}) = 10^{-4}$ ). These latter two results are probably artifacts of the techniques. They may however yield useful information and provide a guide for subsequent work.

(2) A series of computer calculations were made of the adiabatic temperatures and compositions of the equilibrium burned gases.

TG 376-2

The Johns Hopkins University  
Applied Physics Laboratory  
Silver Spring, Maryland

FLAME INHIBITION R.S. AGC QUARTERLY PROGRESS REPORT,  
15 August 1961 - 31 October 1961.

(1) A temperature profile was measured on the spherical stoichiometric methane-oxygen-argon flame system whose composition structure was reported in TG 331-2.

(2) The diffusion coefficient of the system  $\text{A}-\text{B}$  (trace) was measured at atmospheric pressure over the range 300-1070°K.

(3) An analysis was made of the effect of added  $\text{HBr}$  on fluxes and rates on the stoichiometric methane flame. This indicated that a significant fraction of the reaction occurred on the surface of the ball. The principle effect of the added  $\text{HBr}$  appears to be the shifting of the methane reaction to appreciably higher temperatures.

TG 376-3

The Johns Hopkins University  
Applied Physics Laboratory  
Silver Spring, Maryland

FLAME INHIBITION RESEARCH QUARTERLY PROGRESS REPORT, 1 Lay - 31 July 1961.

(1) A set of composition and temperature profiles was determined for a flat methane-oxygen flame ( $\text{CH}_4 - 0.076, \text{O}_2 - 0.02, \text{P}_2\text{O}_5, \text{CO}_2$ , atm, with and without added  $\text{HBr}$ ). Corrosion was so severe that the burner assembly became unusable. A new teflon-glass-ceramic system including traps to protect the pumps has been designed and is being fabricated.

(2) A program to measure the high-temperature diffusion coefficients for the analysis of the inhibited flames has been started. The apparatus has been activated and tested at 300°K and 500°K on the well-known  $\text{He}-\text{CO}_2$  system.

(3) Scavenger probe studies of radical concentrations in flames have been continued. The use of chlorinated hydrocarbons as scavenger for  $\text{H}$  atoms has been shown to be proportional to  $\text{H}_2$  of oxygen concentration using  $\text{O}_2$  as a scavenger have been made. The efficiency of scavenging appears to be high and may approach 100%.

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NOTE: A yearly summary covering all phases of this work is included in this issue.

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